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CONSTRUCTION AND PERFORMANCE OF PLATINUM PROBES FOR MEASUREMENT--ETC(U)
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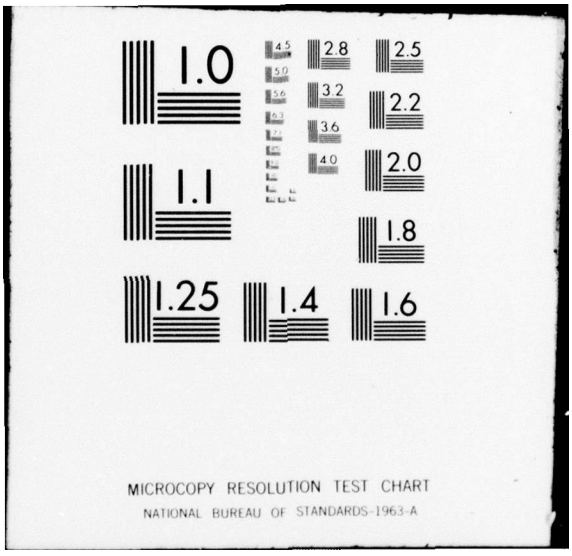
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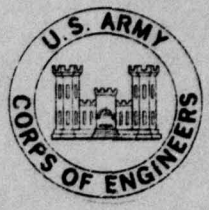

CONSTRUCTION AND PERFORMANCE OF PLATINUM PROBES FOR MEASUREMENTS OF REDOX POTENTIAL

B.J. Blake, B.E. Brockett and I.K. Iskandar

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A simple method is described for construction and testing of platinum oxidation-reduction probes in the laboratory. The probes are 'blacked' with platinic chloride to increase their lifetime. Methods of standardization and problems encountered are discussed.

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PREFACE

This report was prepared by Bethany Blake and Bruce Brockett, Physical Sciences Technicians, and Dr. I.K. Iskandar, Research Chemist, of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by Corps of Engineers Civil Works Research and Investigation Project CWIS 31314, Nitrogen Transformations in Land Treatment.

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The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

INTRODUCTION

The purpose of this report is to describe in detail the procedure used to construct platinum redox probes, the performance of the assembled probes, and the materials used. These probes are being used in lysimeter and laboratory studies associated with the denitrification research program at CRREL.

BUILDING REDOX PROBES

The general plan of the redox probes constructed at CRREL (Fig. 1) is similar to that of Ku (1975). The probe consists of platinum and copper wire soldered together with silver alloy and passed through glass capillary tubing so that the platinum protrudes at one end. The following steps have been successfully used at CRREL to build good platinum probes.

Length of wire

Surface area rather than wire length is the important criterion. Ku (1975) reported that his electrodes had a surface area of exposed platinum of about 0.162 cm^2, using #20 gauge wire.

In the present study the platinum wire is #22 gauge, which has a diameter of 0.064 cm. Using the formula for the surface area of a cylinder, $2\pi rh$, the length of wire needed to create a 0.162-cm^2 exposed area is 1.249 cm (about 1/2 in.).

Since some of the platinum wire will be enclosed within the glass tubing, it is advisable to cut the platinum wire in lengths of 3/4 in. The copper wire should be long enough to conveniently connect the electrode to a pH/mV meter. Approximately 4 in. of glass tubing is needed. About 3 in. of insulation should be stripped from one end of each copper wire.

Silver soldering

A micro-manipulator is needed to hold the ends of the platinum and copper wires together. A small gas-oxygen torch is used for soldering these wires together. The green knob on the side of the hand torch regulates oxygen flow, and the red knob opposite regulates gas flow. (Be sure that the gases are properly connected.) By adjusting these knobs, a small, blue flame should be made intense enough to have just a trace of orange flame at the tip. Be careful of combustible items, especially the gas hoses, and know where the fire extinguisher is. Safety glasses should always be worn when working with the flame.

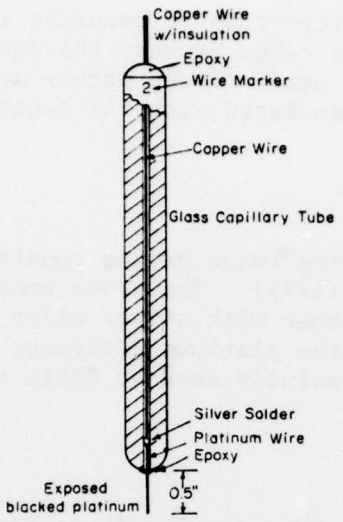

Figure 1. Platinum probe for measurement of oxidation-reduction potential.

Place the platinum and copper wire in each opposing head of the micro-manipulator, and align the ends of the wires until they are touching.

About an 8-in. length of silver solder is convenient to use. Place the tip of the silver solder carefully on top of the platinum-copper joint, and bring the flame under the joint. The silver will flow more uniformly if it is dipped first in silver solder flux. Use just the tip of the flame, so that the copper wire does not overheat. Heat only until the silver solder forms a small bead across the joint. Then the silver solder should be lifted away and the flame removed. A large bead of silver solder at the joint is not desirable, as it will not fit into the capillary tubing. If a large bead is produced, it can be resoldered by holding the platinum wire with pliers (near the soldered end so that the scratches from the pliers will not be on the exposed surface) and heating the joint (flux on the joint will help). The copper wire will fall away. If the silver solder bead goes with it, it can be clipped from the end of the copper wire and a new joint can be made. If the silver stays on the platinum, continue heating until it becomes liquid. Then hit the end of the pliers hard against the counter and the solder will drop off.

The silver solder will melt better if the used tip is clipped off between each soldering operation and flux is used each time it is heated

or reheated. A good joint should be smooth with just a small bead of the silver solder.

The wires should be soaked overnight in a base solution to remove the flux. If the joint is made successfully, it will hold under the stress of a slight pull.

Glass tubing

Capillary Pyrex tubing was selected for this project because of its strength and rigidity. The O.D. (outside diameter) is not critical and can be selected as project designs dictate. The important thing is that the I.D. (inside diameter) be large enough to allow passage of the wire and the soldered joint. Four-inch sections of glass tubing were used in this application. To cut these lengths, the glass was scored with a file, and a drop of water was applied to the fresh scratch before breaking the tubing.

The wire is passed through the tubing until just over 1/2 in. of the platinum protrudes from the end. If the copper insulation does not fit into the tube, it will have to be stripped back farther. (The exposed areas can be covered with heat-shrink insulation later.)

The end of the capillary tube is sealed to the platinum wire using a large hand torch which is secured upright on a ring stand. A measuring instrument (such as a caliper) is placed beside it (also vertical). The platinum end of the capillary tube is carefully rotated in the flame until it has melted and sealed around the wire, leaving a rounded end. It's important that the melted glass does not run down the platinum wire which would shorten the exposed length to less than 1/2 in. The hot tube should be cooled on an asbestos pad or other noncombustible surface.

Care should be taken to avoid melting the platinum wire with the flame. Although the melting point of platinum is much higher than the melting point of glass, a prolonged exposure to the hot inner flame will cause the platinum-copper wire joint inside to separate.

Melting the end of the capillary tubing around the platinum wire often does not produce a leak-free seal. The end of the glass must be carefully sealed with epoxy to prevent cross-contamination.

The best method of sealing is to connect the copper wire end of the probe to a vacuum pump and apply the epoxy around the base of the exposed platinum wire. The vacuum should suck the epoxy into the opening enough to seal any leak. Epoxy with a low viscosity is best. For this project, Armstrong C-7 Resin with Activator W was used. It is important to try to get as little epoxy as possible in contact with the exposed platinum wire.

To dry, the electrodes should be set vertically, platinum end up. If put in an oven (about 40°C) they dry in about an hour. To check for a good seal (after drying), the electrode can be reconnected to the vacuum and the epoxied end placed in water.

The copper end of the tubing must also be sealed. A more viscous epoxy is better for this larger opening. It can be applied around the base of the copper wire with a plastic disposable syringe. The electrodes are set vertically to dry overnight.

Other redox probes have been constructed using "soft" thin-walled glass tubing instead of stronger Pyrex capillary tubing. It was shown by vacuum-testing that epoxy is not necessary for sealing the platinum wire if this type of tubing is used, as the glass itself will form a leak-free seal when heated. This can be accomplished if the thermal expansion coefficient (β) of the glass is greater than or near that of platinum, so that after the glass is melted at the tip of the probe, it cools and forms a shrink fit around the platinum wire. If β glass < β wire by a large gradient, upon cooling the wire will shrink more than the glass, pulling away from it and breaking the seal. Thermal expansion coefficient values for platinum and different types of glass can be found in most handbooks of chemistry and physics (note that the values vary with temperature).

Clipping

The exposed length of platinum is measured to the nearest 1/10 in. It is best to do this after the epoxying, as epoxy on the wire base will shorten the exposed area. A pair of sharp wire clippers will easily trim any excess.

Numbering

Numbering is accomplished by attaching numbered wire markers either to the copper wire or to the top of the glass tubing. If on the glass tubing, the markers should be further secured with cellophane tape.

Platinum blacking

The purpose of the blacking is to prevent the formation of air bubbles on the platinum wire when in solution, which would interfere with the proper electrode reading. Platinum electrodes before blacking gave lower readings for pH 4 (+160, +177) except when they were electro-cleaned (198, 206, 213 mV) and the readings were difficult to stabilize on the pH/mV meter. For pH 7, the readings were higher on the unblacked probes both without electro-cleaning (+20, +30, +49) and with it (+19, +32)*.

*Compare with Tables on pp. 7 and 8

Written instructions are given with the platinum-blacking kit - a 4 1/2 volt battery unit (Model PK-1A) available through Beckman Instruments, Inc. The electrodes are first electro-cleaned by attaching them, two at a time, to the binding posts (that is, one at each post) and immersing the platinum ends in HCl (30 ml of conc. HCl in 70 ml distilled water). A rheostat is used to adjust the current to 125 mA on the ammeter for 6 min, reversing polarity every 60 sec. with the reversing switch. These are then removed from the kit and rinsed for 2-3 min. in running water (hot is best). The electrodes are then reattached to the binding posts and immersed in platinizing solution at 25 mA for 2 min, with the polarity reversed every 15 sec. When removed, the platinum wire should have a smooth black coating. If the blacking is not uniform it must be redone - it should be wiped off, electro-cleaned, and reblacked. Once blacked, the platinum tips must be kept in distilled water until used.

If there is no available platinizing solution, it can be made by dissolving 3 g of chloroplatinic acid and 0.02 g of lead acetate in 100 ml of distilled water. All work with the kit and HCl should be done under a hood. Avoid scratching the platinum black coating.

Standardization

Buffer solutions of pH 4 and pH 7 are used to measure the redox potential using a saturated calomel probe as a reference electrode. Approximately 0.5-1.0 g of quinhydrone (or hydroquinone) must be added to 100 ml of the buffer and the solution stirred while readings are taken. On the pH/mV meter, the calomel electrode should be connected to the reference post and the platinum electrode should be attached to the positive post. Table I summarizes the data obtained using blacked electrodes.

Some unblacked electrodes can also be used for redox potential measurements. These will generally read higher for awhile if they are electro-cleaned first. However, the readings are not very stable.

According to Ku (1975) and Bohn (1971) the electrode should give a reading of +218 mV in pH 4 at 25°C, and +41 mV at pH 7 at 25°C. The readings change slightly with time, usually increasing. It is necessary for all the electrodes to read within 10 mV of each other. If not, they may need reblacking.

PROBLEMS ENCOUNTERED

1. Some resoldering had to be done because the original joint would not fit into the capillary tube.

2. The heat from the glass blowing melted the platinum wire on one electrode and disconnected a weak joint on another.

3. It was not discovered until after the electrodes were completed that they leaked at the platinum end. They had to have the water removed and the epoxy applied. The drying destroyed the effect of the blacking, and each electrode had to be reblacked.

4. The readings on the pH/mV meter were very low at first because the hydroquinone was not added to the pH solution.

5. Out of 72 electrodes, 4 were damaged in the process of construction.

LITERATURE CITED

Bohn, Heinrich L. (1971) Redox potentials. Soil Science, vol. 112, no. 1, p. 39-45.

Ku, W. (1975) Equilibrium adsorption of inorganic phosphate by lake sediments. Thesis, Amherst, University of Massachusetts (unpublished).

Table I. Redox probes - emf (in millivolts) of hydroquinone in pH buffer solutions.

Electrode	pH 4				pH 4		
	June 30*	July 1*	July 8+	July 11+	July 1*	July 2*	July 8+
1		+179	+182		+2.2	+8.1	+12.2
2		+179	+180		+2.0	+8.4	+12.2
3		+180	+180				+10.4
4		+179	+181		+7.6	+5.2	+10.6
5		+179	+185			+9.8	+13.0
6		+180	+186				+12.1
7		+179	+181		+8.3	+4.9	+10.6
8		+178	+181		+3.0	+8.1	+11.9
10		+180	+186	+179			+12.6
11		+179	+181		+3.0		+9.6
12		+179	+186	+181			+12.6
14		+179	+179		+2.0	+8.2	+12.9
15		+179		+183		+8.4	+10.2
16		+178		+183		+8.4	+10.2
18	+165	+179	+185				+12.3
20	+165	+180	+180			+9.6	+12.9
21		+179	+180		+3.4	+8.4	+12.2
22		+179	+184			+8.7	+11.6
24		+179	+182	+181			+13.2
25				+181			+13.5
26		+178	+181		+2.1	+8.6	+12.1
27		+179	+182				+12.1
28		+180	+181		+2.4	+7.5	+12.4
29		+178	+181				+9.6
30		+179	+185	+180			+10.7
31		+178	+180		+8.3		+13.3
32		+180	+180		+8.8		+12.7
33		+178	+180		+8.5	+6.2	+11.9
34		+179	+182		+8.7	+12.0	
Average	165	179	182	181	5.0	8.0	11.8

Table I. (Continued)

Electrode	pH 4 June 30*	pH 4 July 1*	pH 4 July 8+	pH 4 July 11+	pH 4 July 1*	pH 4 July 2*	pH 4 July 8+
38		+180	+186	+182			+12.0
39	+166	+180	+185				+12.2
40		+179	+181				+11.8
41		+178	+181				+10.0
42		+178	+181		+8.6	+7.4	+12.0
43	+171	+180	+181				+11.6
44		+179	+183		+6.9	+8.7	+11.3
45		+180	+180			+8.9	+12.8
47		+180	+183				+9.4
48		+179	+179			+8.8	+12.8
50		+178	+180			+8.5	+10.2
51		+179	+180				+11.6
52	+165	+180	+181			+10.1	+12.6
53			+180				+11.6
54	+165	+180	+179				+12.0
55	+165	+181	+179			+12.9	+10.5
56	+164	+180	+180			+9.1	+9.4
57		+179	+180			+7.7	+13.5
58	+165	+180	+180			+9.0	+12.6
59		+179	+180		+7.0	+8.6	+11.8
60		+179	+185				+9.7
61		+179	+181		+2.2	+8.2	+10.5
62		+179	+183			+8.7	+11.5
63		+179	+180		+2.5	+7.9	+9.7
64		+179	+184				+12.8
65		+178	+182		+1.8		+11.5
66		+179	+180				+12.7
67		+180	+179		+7.2	+8.6	+12.7
68			+180				+12.5
69	+167	+182	+180			+8.5	+9.6
70		+180	+180				+12.4
71		+178	+181				+12.0
Average	166	179	181	181.5	5.1	10.9	11.5

*Readings obtained after the first platinum-blacking of the probes.

+Readings obtained after the probes had been platinum-blacked a second time (the original blacking was damaged when leaks in the glass tubing were repaired).

Electrode numbers omitted correspond to probes which were damaged or left unblacked.